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DEPARTMENT OF CERAMICS

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A CHEAP ENAMEL FOR STONEWARE

PART II.

By

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A CHEAP ENAMEL FOR STONEWARE.

Part II.

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The last contribution of "A Cheap Enamel for Stoneware," in Vol. X, was sent in for publication three days after the last trials came from the kiln. The most promising enamels of the work done up to that time were the members of Series IX, and the best one of the series was No. 35.

As has been noted, no craze marks were observed on No. 35, when taken from the kiln. After three weeks' time a craze mark appeared on the bottom of one trial. Crazing has been going on gradually until now the trials are completely checkered with craze marks. The author is of the opinion that the crazing is due to the softness of the body rather than to the glaze itself, since the trials were burned at cone 01.

SERIES X.

The maturing temperature of No. 35 is altogether too low for the stoneware body and too high for other types of ware, notably those maturing at cone 04. Hence it was thought advisable to construct a series starting with a glaze of the same type as No. 35, but which should be more fusible. The RO, Al_2O_3 and P_2O_5, which are the same as those in No. 35, are kept constant throughout the series, the two variable members being SiO_2 and B_2O_3.

Each succeeding member has the B_2O_3 decreased one tenth and the SiO_2 increased accordingly. Two fritts were

made for Series X, which have the following formulae and batch weights:

Fritt G.

Formula			*Batch weights*	
.8571 CaO	.357 Al_2O_3	2.3 SiO_2	Bone Ash	30.75
.1429 ZnO		.2857 P_2O_5	Zinc Oxide	4.03
			N. C. Kaolin	32.09
			Flint	33.13

Fritt H.

Formula			*Batch weights*	
.25 K_2O	.5625 Al_2O_3	2.125 SiO_2	Feldspar	30.80
.75 CaO		.250 P_2O_5	Bone Ash	17.09
		1.250 B_2O_3	N. C. Kaolin	17.83
			Boracic Acid	34.28

Fritt G was calcined in a flinted sagger at cone 8. Fritt H was fused in a flinted crucible and quenched in water. Both fritts were ground dry to a fine powder ready for weighing.

Glazes.

	Formulae							*Batch weights*					
Glaze No.	K_2O	CaO	Zno	Al_2O_3	SiO_2	P_2O_5	B_2O_3	Brandywine Feldspar	Fritt G	Fritt H	Zinc Oxide	Georgia Kaolin	Flint
36	.2	.6	.2	.55	2.3	.2	1.0	.....	.....	81.90	4.45	7.07	6.58
37	"	"	"	"	2.4	"	.9	3.06	5.28	73.91	4.24	7.09	6.42
38	"	"	"	"	2.5	"	.8	6.14	10.60	65.88	4.02	7.11	6.25
39	"	"	"	"	2.6	"	.7	9.24	15.94	57.80	3.81	7.13	6.08
40	"	"	"	"	2.7	"	.6	12.35	21.31	49.68	3.59	7.15	5.92
41	"	"	"	"	2.8	"	.5	15.48	26.71	41.51	3.38	7.17	5.75
42	"	"	"	"	2.9	"	.4	18.63	32.14	33.30	3.16	7.19	5.58
43	"	"	"	"	3.0	"	.3	21.79	37.60	25.04	2.94	7.21	5.42
44	"	"	"	"	3.1	"	.2	24.79	43.09	16.74	2.72	7.23	5.25
45	"	"	"	"	3.2	"	.1	28.17	48.60	8.39	2.51	7.25	5.08
46	"	"	"	"	3.3	"	.0	31.39	54.16	.....	2.28	7.27	4.90

These glazes were applied to bone dry stoneware crocks but flaked so badly on drying that the series was abandoned. A few subsequent dips of the two extremes of this series (Nos. 36 and 46) worked very satisfactorily on biscuit. No further investigation was made into the working qualities of the members of this series on biscuit since the work is mainly along the line of single fire enamels.

SERIES XI.

Series X was modified in series XI to overcome flaking. In this series the same formulae are used as in series X, the difference being that in series XI the raw clay is increased from 0.1 to 0.15 and Tennessee ball clay No. 3 is used in place of Georgia kaolin. This required the making of two new fritts (I and J), since the excess clay above 0.1 in series X was fritted.

Fritt I.

Formula	*Batch weights*	
$\left.\begin{matrix}.5\ K_2O \\ .5\ ZnO\end{matrix}\right\}\ .5\ Al_2O_3 \left\{\begin{matrix}3.0\ SiO_2 \\ 2.5\ B_2O_3\end{matrix}\right.$	Brandywine Feldspar	44.28
	Zinc Oxide	6.44
	Boracic Acid	49.28
Combined weight 494.		

Fritt J.

Formula	*Batch weights*	
$1.0\ CaO\ \ .3\frac{1}{3}\ Al_2O_3 \left\{\begin{matrix}1.3\frac{1}{3}\ SiO_2 \\ .3\frac{1}{3}\ P_2O_5\end{matrix}\right.$	Bone Ash	45.06
	N. C. Kaolin	37.50
	Flint	17.44

The first one was drop fritted while the latter was calcined to cone 8 in a flinted sagger. Both were reduced to powder and used in this form in weighing up the glazes.

Batch Weights Series XI (Having the same successive formulae as Series X).

Glaze	Brandywine Feldspar	Fritt I	Fritt J	Zinc Oxide	Tenn. Ball Clay No. 3	Flint
47	....	53.89	35.56	....	10.55	....
48	3.05	48.63	35.66	0.44	10.58	1.64
49	6.11	43.35	35.75	0.89	10.61	3.29
50	9.19	38.03	35.85	1.34	10.64	4.95
51	12.28	32.69	35.95	1.79	10.67	6.62
52	15.40	27.32	36.05	2.24	10.70	8.29
53	18.53	21.91	36.15	2.70	10.73	9.98
54	21.68	16.48	36.25	3.15	10.76	11.68
55	24.85	11.02	36.35	3.61	10.79	13.38
56	28.03	5.52	36.46	4.08	10.82	15.09
57	31.23	....	36.56	4.54	10.85	16.82

Three burns were made of the members of this series. The first four members were burned to cone 04, the first six to cone 01, and all were burned to cone 6.

Cone 04 Burn.

No. 47 in this burn appeared to be well matured and glossy. It was not quite so opaque nor light colored as No. 35 (see p. 239 and p. 241, Vol. X, *Trans. A. C. S.*). A few small bubbles appear on the exposed rim. The glaze crazes some on the soft buff body.

No. 48 is the best glaze of the burn, though it has a very slight tendency to pull away from the rim. It is nearly as opaque and light in color as No. 35. It crazes some.

No. 49 (having the same formula as No. 35) is underfired, being a little dull in texture. It is opaque and nearly white, crazes.

No. 50 is decidedly underfired, having the appearance of highly vitrified porcelain. Badly crazed. In two places the glaze has loosened and stands out from the body.

Cone 01 Burn.

No. 47 is glossy, but the opacity has decreased, giving a translucent glaze. Bubbling has also increased, crazing decreased.

The opacity of No. 48 has also diminished. The glaze in this burn is otherwise good.

No. 49 is opaque but not quite so light colored as No. 35. A slight tendency to flake appears. The glaze shows a few craze marks.

No. 50 is more opaque than 49 though not quite so glossy. Crazes badly.

Nos. 51 and 52 are underfired and crazed.

Cone 6 Burn.

In this burn all glazes show small bubbles up to No. 55. No. 47 is bubbled the worst, having a frothlike appearance. Bubbling decreases towards No. 55. No. 55 has a pitted appearance. These glazes are undoubtedly overfired.

No. 56 is well matured and shows no bad defects. Its whiteness is a little better than that of a good bristol.

No. 57 is a little whiter than 56 though not brilliant enough to be a good glaze. It would be better at cone 7.

Conclusions on Series XI.

The glazes of this series are capable of producing glossy opaque enamels when given the right heat treatment. If a little underfired, they are dry and dull. When slightly overfired, they lose opacity and begin to develop bubbling. The range of temperature is very short, not over $1\frac{1}{2}$ cones at most. For this reason they are not commercially valuable.

The writer's practical experience in glazes in which magnesite was used, brought out the fact that MgO possessed strong opacifying properties. Tin enamels containing 0.25 MgO required less tin oxide in order to produce the same degree of opacity than those containing no MgO. It was also observed in testing feldspars that soda feldspar of a pure grade fused to a whiter and more opaque bead than potash spar. The crystalline form of soda spar generally occurs as a porcelain white mineral called Albite; potash spar, or Orthoclase, on the other hand, is more translucent and dark in color.

If it is true concerning bases belonging to the same chemical group or family that those of low molecular weight possess a lower degree of solubility in a silicate fusion and a higher velocity of crystallization than bases of high molecular weight, then less molecular quantities of Na_2O and MgO would be required to produce "supersaturation" and "incipient crystallization" than the bases of their corresponding groups having higher molecular weights, namely K_2O and CaO.

Acting upon the above suggestions, series XII and XIII were constructed. It will be noted that the members of these series are glazes of the bristol type, in which Na_2O is substituted for K_2O and MgO replaces CaO. In these two series the RO is kept constant.

SERIES XII.

Formulae						*Batch weights*				
Glaze	Na_2O	MgO	ZnO	Al_2O_3	SiO_2	Soda Feldspar	Grecian Magnesite	Zinc Oxide	Tenn. Ball Clay No. 1	Flint
58	.3⅓	.3⅓	.3⅓	.4⅓	2.2	68.37	10.96	10.57	10.10	.....
59	"	"	"	"	2.5	63.88	10.24	9.87	9.43	6.58
60	"	"	"	"	2.8	59.94	9.60	9.26	8.85	12.35
61	"	"	"	"	3.1	56.45	9.05	8.72	8.33	17.45
62	"	"	"	"	3.4	53.34	8.55	8.25	7.88	21.98
63	"	"	"	"	3.7	50.56	8.10	7.82	7.47	26.05

SERIES XIII.

Formulae						Batch weights				
Glaze	Na_2O	MgO	ZnO	Al_2O_3	SiO_2	Soda Feldspar	Grecian Magnesite	Zinc Oxide	Tenn. Ball Clay No. 1	Flint
64	.3⅓	.3⅓	.3⅓	.5	2.3⅓	64.06	10.27	9.90	15.77	.....
65	"	"	"	"	2.6⅓	60.10	9.63	9.29	14.79	6.19
66	"	"	"	"	2.9⅓	56.59	9.07	8.75	13.93	11.66
67	"	"	"	"	3.2⅓	53.48	8.57	8.26	13.16	16.53
68	"	"	"	"	3.5⅓	50.68	8.12	7.83	12.48	20.89
69	"	"	"	"	3.8⅓	48.17	7.72	7.44	11.86	24.81

These glazes were applied to bone dry stoneware trials and fired to cone 8. They were taken from the kiln while still quite hot. None of them show any signs of crazing. There is very little difference in the whiteness of the members of the two series. All are as opaque and white as a good tin enamel. Nos. 58 and 64 are a little dull. Glossiness increases with increase in SiO_2. The glossiness of Nos. 60 to 63 and 66 to 69 are very good and in this respect will compare favorably with the majority of stoneware glazes on the market and are far superior to them in whiteness. All five pieces of No. 62 are especially good. All members of Series XII have a slight tendency to bead where the glaze is too thick. The glazes do not show any tendency to pull away from the corners and edges. The small beading tendency can be overcome by the addition of borax.

In Series XIII in which the Al_2O_3 is increased the beading has increased a little. The glazes do not appear to be quite so fusible. Otherwise they are good.

In order to compare the opacifying effect of MgO with that of ZnO, the following series was prepared by the class in glaze making in their regular laboratory work. In this series (Series XIV) a glaze of the Bristol type was selected for the first member. In each succeeding one 0.1 MgO replaces 0.1 ZnO, all other members remaining constant.

SERIES XIV.

Formulae							Batch weights					
Glaze	K_2O	CaO	ZnO	MgO	Al_2O_3	SiO_2	Potash Feldspar	Whiting	Tenn. Ball Clay No. 1	Grecian Magnesite	Zinc Oxide	Flint
H-1	.3	.2	.5	.0	.5	4.0	167.1	20.0	51.6	....	40.5	128.0
H-2	"	"	.4	.1	"	"	"	"	"	8.4	32.4	"
H-3	"	"	.3	.2	"	"	"	"	"	16.8	24.3	"
H-4	"	"	.2	.3	"	"	"	"	"	25.2	16.2	"
H-5	"	"	.1	.4	"	"	"	"	"	33.6	8.1	"
H-6	"	"	.0	.5	"	"	"	"	"	42.0	....	"

These glazes were applied to small bone dry stoneware crocks and fired to cone 7 in 25 hours.

There is but little difference in the appearance of the members of this series. If anything, H-6 is a little the whitest and smoothest in texture. No bad defects appear. The conclusion which we may draw from the appearance of the trials is that MgO is at least equally as good an opacifier as the same molecular quantity of ZnO.

DISCUSSION.

Mr. Stull: Referring to the trials will say that I have brought only two, No. 35 representing the most promising enamel of last year's work and No. 62 which is the most promising one to date. You will notice that No. 35 is a sort of ivory color and matures altogether too low for stoneware. The trials were nested, and happened to touch at this point (indicating) where a bubble formed, hence this bubble near the rim is not really a defect of the glaze in itself. You will notice that the enamel is badly crazed, and has a little tendency to flake though not bad enough to be serious. No. 62 is a member from Series XII. You will notice in the bottom where the glaze is thick, it beaded in one spot and partially healed over again. Those who have had experience in Bristol glazes will agree with me that the beading is not bad, since no "dope" was added to these glazes to prevent it.

There is a great field open for investigation to determine the opacifying effects of different materials. We have evidence that magnesia is a good opacifier; a good grade of magnesite when properly used in conjunction with zinc oxide will give whiter and glossier effects than the regular type of Bristol glaze.

Mr. Purdy: Those of us who have had experience along this line note with interest the discussion of the opacifying effect of Na_2O as against K_2O, and Mgo as against CaO, in conjunction with zinc.

Mr. Jackson: In regard to the trial passed around, I notice two temperatures mentioned, for instance, cone 01 and cone 8. I am not very familiar with the stoneware business, but I would like to ask whether it is customary to have two fires, a biscuit and glost? Do I understand that the piece going around had a previous biscuit fire?

Mr. Stull: No, sir.

Mr. Purdy: There is only one part of the country that I know of where they use two fires, and that is in the West where they have clays of enormous shrinkage.

Mr. Jackson: Is it practicable and customary to make stoneware as low as 01?

Mr. Purdy: It is not customary; it might be practicable.

Mr. Stull: I am sure there is no true stoneware made in this country as low as 01; but I am sure that terra cotta is made even as low as cone 05 where a slip and enamel are applied to the bone dry ware and matured in one burn, which is a much more difficult problem.

Mr. Purdy: Bristol glaze type?

Mr. Stull: No. sir; an underglaze coating or slip, and white tin enamel or glaze applied over it and all matured in one burn. If it can be done on large pieces, I do not see why it could not be done on small pieces.

Mr. Purdy: Is this over-spray a raw leadless glaze?

Mr. Stull: No sir, a raw lead glaze not a leadless glaze.

Mr. Purdy: That is another question. I do not call that a Bristol glaze. We must be careful to keep Bristol glaze apart from lead glazes because it has different properties.

Mr. Jackson: The point I was getting at is how large a field the one-fire proposition covers so far as a stoneware body is concerned. I do not call any glaze carrying boric acid a Bristol glaze.

Mr. Purdy: You are wrong.

Mr. Jackson: That is the idea I had. Is the boric acid fritted?

Mr. Stull: Yes, sir, it is in series ten and eleven.

Mr. Jackson: I would like to ask Prof. Orton if I am right in what I said. When a glaze carries boric acid fritted in it, can it properly be called a Bristol glaze?

Mr. Orton: It does not meet the idea of a Bristol glaze that I have been teaching. A Bristol glaze is supposed to be a raw glaze. However, this glaze under discussion might be a type which we could afford to use in place of the old raw Bristol glaze. I do not know about that.

Mr. Jackson: That is as I understood it. The glaze at the top of the list on the blackboard is of the Bristol glaze type as I understand it.

Mr. Orton: It is a little too high in silica for a typical Bristol glaze.

Mr. Stull: I am afraid a great many are of the opinion that this work is along the line of Bristol glazes. That is not the line of inquiry, but a cheap enamel for stoneware as indicated by the title on the program. The main object of the investigation is to produce a cheap enamel for the lower grades of ware which will be a fairly good substitute for tin enamel; not only for stoneware but for other types of ware maturing at lower temperatures. That does not confine the investigator to one type of glaze. It is a broad field to work in. I am sorry I have not been able to do more work in this line of experimentation.

Mr. Fuller: What do you mean by "dope" to keep the glaze from crawling?

Mr. Stull: Nearly all stoneware glazes have a tendency to crawl or bead because they are highly viscous. In order to prevent this crawling it is customary for potters to use such materials as plaster of paris, borax, carbonate of soda, or some other soluble salt in their glazes. Exactly what action these soluble salts have upon the glaze has not been definitely determined. My opinion is that in the case of borax and carbonate of soda, these materials not only serve to hold the glaze to the bone dry body after dipping but also fuse in the early stage of burning forming a sticky matrix which prevents the glaze from curling up, which precedes beading.

Mr. Stephani: I would like to say that I have had some experience in the terra cotta line with beading and crawling, and my impression is that there are two kinds. We get one by getting the slip or glaze too heavy on the ware and the consequence is one or the other cracks in drying before it goes into the kiln, and when the glaze begins to fuse it beads and crawls; and in the other case we get an effect which does not appear before it goes into the kiln. I think manufacturers, as a rule, for the first kind of beading, use a material something like calcium sulphate, and some use glue to hold the glaze together in drying, making it tougher. For the second kind, the kind happening in the kiln and which does not show up in the drying, boracic acid is used; or, in a terra cotta glaze the ZnO is reduced with MgO. The latter fault is due to imperfect glaze, while the former can be overcome mechanically, i. e. by applying the underslip or glaze thinner.

Mr. Fackt: May I ask Mr. Stephani whether he has used Cornwall stone in place of the feldspar to prevent the crawling and cracking which he speaks of as happening before the ware goes into the kiln?

Mr. Stephani: I never used Cornwall stone in any glaze; but I find the best way to overcome that effect is by remedying the underslip, or putting less of it on the ware.

Mr. Miller: Mr. Stull tells us he finds an improvement in color by substituting magnesium for tin.

Mr. Purdy: The substitution of magnesium for what?

Mr. Stull: An improvement in color by substituting magnesium oxide for zinc oxide. It does make a little difference in the fusibility. Glazes containing MgO are not quite so fusible as glazes containing ZnO, other things being equal. Dr. Simonis, in his work on cones, in which he used magnesium oxide, points out that the action of the MgO in the cones is to hold the cones up to a certain point when the fusion is comparatively sudden. It is claimed for that reason that they are better indicators of temperature than the regular Seger cones. We are getting more light all the time as to the action of MgO in ceramic mixtures. In fact, we do not yet know all of its possibilities. The magnesite which I used was rather a pure variety obtained from the Foote Mineral Company. I am told that a good variety of the Grecian magnesite is delivered in New York for about twenty-four dollars a ton. If it can be used successfully it will cheapen enamels wonderfully and fill a long felt want for the lower grades of ware.

Mr. Frink: One thing has occurred to me in regard to this discussion of magnesia. Magnesia is used in glass to some extent, usually being found as an impurity in the lime, and experiments have been made which show that the viscosity is very much reduced thereby.

Mr. Purdy: The viscosity is reduced?

Mr. Frink: Yes. That bears out what the gentleman has said. When the temperature rises to a certain point, liquefaction is reached more rapidly. Does not the similar action of borax account for the beneficial results of this material in the case of crawling or beading, because of the filling of the interstices with liquid?

Mr. Purdy: Was it used in a small pot or a big batch?

Mr. Frink: I have experimented with it in tank of capacity of 600 tons, and also with quantities of fifty or sixty pounds.

Mr. Purdy: The viscosity seemed to be the same in both instances?

Mr. Frink: Yes.

Mr. Purdy: What was the effect of magnesia on devitrification?

Mr. Frink: That seems to vary according to conditions, under which it is melted. If melted under a high reducing flame devitrification takes place slowly; but under a high oxidizing flame it takes place rapidly.

Mr. Purdy: Is that peculiar of your magnesium glasses or is it true also of lime glasses?

Mr. Frink: Yes; it is also true as to lime glasses; but with the magnesium glasses it is particularly so and I attribute it to the more liquid condition. That is my theory.

Mr. Purdy: We have to have equivalent of devitrification to have opacity.

Mr. Frink: Yes; and I imagine if you put that under oxidizing conditions you will get that more rapidly.

Mr. Purdy: I will ask Mr. Stull if magnesium in the form of light, fluffy oxide has the same effect as when introduced as magnesite?

Mr. Stull: I have never used the light commercial magnesia only in a fritt on one or two occasions, and have never made any comparisons between it and the mineral magnesite. Commercial magnesia is comparatively expensive. We can obtain magnesite which will analyze very high in $MgCO_3$, with very little impurity which would cause discoloration. There is a deposit in California which is claimed by some to be better than the Grecian, but the cost of mining it and shipping it east is greater. By a little sorting, a comparatively pure grade can be had as low as thirty to forty dollars a ton.

Mr. Purdy: I asked that question in the interest of Hottinger, Barringer, and Hull.

Mr. Stull: What is the effect of magnesia upon iron color in glass? In series twelve and thirteen Tennessee ball clay was used, yet the glazes do not show any trace of cream color.

Mr. Frink: It is so contradictory in action that I cannot answer the question definitely. We sometimes get one effect and sometimes another. I think this is a matter of oxidizing and reducing conditions. It seems to me you would get better results if steam were thrown into the kiln. It seems you have a condition analagous with that prevailing in a lime kiln. I made some experiments one time, introducing steam into a lime furnace. It was found that devitrification was very much enhanced. There are two forms of devitrification, one due to pressure and the other to oxidation. Pure oxygen will produce devitrification.

Mr. Purdy: I note that Mr. Stull did not draw any conclusions in regard to soda or potash feldspar, as fluxes in these glazes.

Mr. Stull: As yet no experiments have been made in this line to determine that. This will probably be investigated later.